

THE UTILITY OF PHENOL-ALDEHYDE CROSS LINKING RESINS IN
POLYMER MODIFIED ASPHALT - THE BUTAPHALT(tm) PROCESS

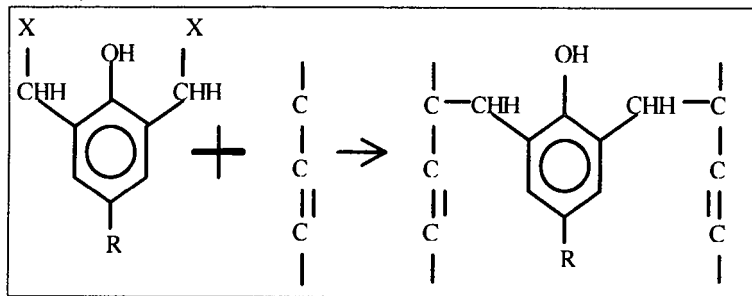
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The use of Phenol-Aldehyde cross linking or vulcanizing resin is well known in the rubber and plastics industry. Previous to our work little (if any) understanding of the utility of these compounds in polymer modified asphalt (or bitumen) was known. This presentation will hopefully enlighten practitioners of the art of asphalt modification on this subject. This art is commercially known as the Butaphalt(tm) Process.

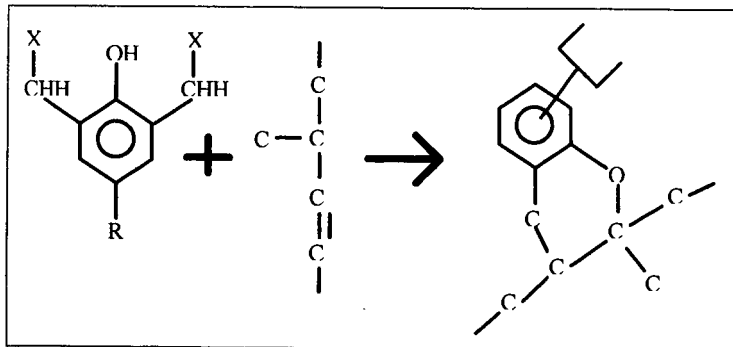
Of initial interest is the mechanism of reaction of Phenol-Aldehyde cross linking resins. As the quantitative analysis of such a mechanism in asphalt would likely need years of effort to resolve, we will look at possible mechanisms in a rubber system. Several publications offer excellent discussions on the art of vulcanization. Science and Technology of Rubber, Second Edition, edited by James E. Mark, et. al., Academic Press, page 366, is such a publication. Therefore, a possible mechanism is illustrated in Figure 1 below.

Figure 1



Another possible mechanism for the reactive phenolic resins involves the formation of a quinone across the double bond of the rubber molecule. Again, several sources of information in the literature are available. Science and Technology of Rubber, Second Edition, edited by James E. Mark, et. al., Academic Press, page 368, makes such reference. This mechanism is thought to create a chroman or chromane structure. This chroman(e) structure is illustrated in Figure 2 below.

Figure 2



Evidence of some form of a chemical and resulting physical change has taken place in the asphalt can be observed by testing Conventional (abbreviated as Cnvntal in tables below) and Butaphalt(tm) Processing. Such a test program with Lloydminster asphalt was performed. It should be noted that this asphalt is generally considered to be a good to excellent candidate for polymer modification. These select tests and their results are also compared at various concentrations of a commercially available high molecular weight radial styrene butadiene styrene (SBS) polymer. Test results are given in Table 1 below.

Table 1

Tests Results in Celsius	3.50% SBS Cnvntal	3.50% SBS Butaphalt	2.50% SBS Cnvntal	2.50% SBS Butaphalt
Separation @ 162	16.11	-0.14	15.14	-0.14
SoftPt B/4 TFOT	70.00	79.44	54.31	58.33
SoftPt Aft TFOT	50.97	63.89	49.17	56.67
B/4-Aft Soft Pt	-19.03	-15.55	-5.14	-1.66

The Separation Test involved static heated storage for each specimen for 48 hours. Although Lloydminster asphalt is normally considered very good for modification, the Separation value is unacceptable under the Conventional Process. However the Butaphalt(tm) Process corrected this deficiency completely. Notice that these results are independent of the SBS concentrations.

The Softening points are always higher with the Butaphalt Process (tm) for a given polymer level. This is true whether observing these results either before or after the Thin Film Oven Test. The Butaphalt(tm) Process consistently yielded minimum decrease Softening Point differential values through the Thin Film Oven Test. These results would indicate longer storage life at in service storage temperatures. These results should also indicate a better product through the hot mix plant and on the road.

We will next look at an asphalt that is considered to be a "problem" for polymer modification. This asphalt is known to be from a wide variety of combined crude oil feed stocks. Among the possible crude oil selections is Alaskan North Slope. Asphalt made from or containing significant quantities of Alaskan North Slope crude oil have been known to have problems when modified with either SBS or styrene butadiene random polymerized latex (SBR) polymers. This next asphalt was not only reported to have significant Alaskan North Slope crude oil but is also reported to have slightly air blown components used in its manufacturing process. Generally speaking, limited air blowing of a asphalt or its component parts will not be severely detrimental to the final traditional product. But, air blowing a asphalt or its component parts are not desirable for a candidate asphalt for polymer modification. We will again examine the Butaphalt(tm) Process in comparison to a Conventional Process in this asphalt. The same high molecular weight SBS polymer at 2.50% by weight dosage level as previously discussed will be used again. In this study, slightly more of the Butaphalt(tm) compound (commercially known as BLC-720 OR B-720) was used over the previous study given above. We will also look at a different set of physical test results. Selecting different physical tests to examine in this study was purposely done to give the reader a better overall understanding of what Phenol-Aldehyde cross linking resins as used by the Butaphalt(tm) Process offer the asphalt polymer formulation. One such physical test that indicates chemical change in polymer modified asphalt is the Force Ductility test. Figure 3 (on the last page) are the Force Ductility curves generated at 4 Celsius, 5 cm/min pull rate from or by the Butaphalt(tm) Process and the Conventional Process. The solid line represents the Butaphalt(tm) Process with its higher initial peak and higher values throughout its elongation. It is the authors opinion that this over all increased value indicates some form of chemical modification to the asphalt polymer composition. It is further the authors opinion that the binder made by the

Butaphalt(tm) Process with these improved Force Ductility values will yield a final product with better overall service life.

Table 2 below gives test results on Ball and Ring Softening Point. Results are given as before and after the Thin Film Oven Test (TFOT).

Table 2

Test (Celsius)	Cnvntal	Butaphalt
Soft Pt B/4 TFOT	51.11	80.56
Soft Pt Aft TFOT	55.00	65.00
B/4-Aft Soft Pt	+3.89	-15.56

In this case, the Butaphalt(tm) Process had higher overall values both before and after the Thin Film Oven Test. The Conventional Process indicated an increasing softening point value through the TFOT with the Butaphalt(tm) Process indicating the opposite trend.

Table 3 below gives test results on ASTM Kinematic Viscosity. Results are given as before and after the Thin Film Oven Test (TFOT). In this table the Percent Change is calculated as $[(B/4 \text{ TFOT}) - (\text{Aft TFOT}) / (B/4 \text{ TFOT})] \times 100$.

Table 3

Kinematic Visc.	Cnvntal	Butaphalt
B/4 TFOT, cStk	495	1500
Aft TFOT, cStk	835	1457
B/4-Aft, cStk	+40	-43
Percent Change	+8.08	-2.87

In this case, the Butaphalt(tm) Process had higher but decreasing values through the TFOT than the Conventional Process. The Butaphalt(tm) Process did have the lowest percent change from the original Kinematic Viscosity.

This same asphalt was also modified with a commercially available SBR latex. The dosage level was 2.50% rubber solids (the same amount as was SBS rubber above) but the amount of Butaphalt(tm) compound BLC-720 was used as with the Lloydminster asphalt of Table 1 above. The process of incorporating the SBR latex into the asphalt is some what proprietary.

The proprietary process of incorporating SBR latex may account for the possibly better than expected Conventional Processing results. This is especially true in Figure 4 (on the last page) illustrating the Force Ductility results. Again, the sample with the Butaphalt(tm) compound BLC-720 (the dashed line) had higher initial peak and overall values. As before, it is the author's opinion that this increased value Butaphalt Process will result in superior binder performance.

As before, we will examine Ring and Ball Softening Point both before and after Thin Film Oven Testing. This work is summarized in Table 4 below.

Table 4

Test (Celsius)	Cnvntal	Butaphalt
Soft Pt B/4 TFOT	51.11	51.11
Soft Pt Aft TFOT	53.33	56.67
B/4-Aft Soft Pt	+2.22	+5.56

Results from this work indicate that this combination of asphalt and SBR latex are equal on initial softening point values. In this case, the Butaphalt(tm) process gave higher values through the TOFT than the Conventional Process. The increase is significant but not to the degree of being detrimental to the product. As a result, the final product in the field may well be very acceptable.

One test parameter that has been historically difficult for SBR latex is Elastic Recoverv (ER). In this studv, the Elastic

Recovery is improved by the Butaphalt(tm) Process over the Conventional Process. Further, the Elastic Recovery value through the TFOT is still acceptable for the Butaphalt(tm) Process. The ER procedure used a standard ductilometer and to elongate the specimen at 5 cm/min at 10 degrees Celsius to 20cm., relax for 5 minutes, cut about the center and leave undisturbed for sixty (60) minutes. The ends were then brought together and the ductilometer reading recorded. The calculation was as follows: $[(\text{initial elongation}) - (\text{final reading}) / (\text{initial elongation})] \times 100 = \text{E R}$. These results are given in Table 5 below.

Table 5

Elastic Recovery	Conventional	Butaphalt
E R B/4 TFOT	53	61
E R Aft TFOT	49	58
B/4-Aft E R	4	3

From this information, one may find that the Butaphalt(tm) Process will allow formulations with improved Elastic Recovery. This improvement could likely mean the difference between acceptable and non acceptable specification product. The change in E R from before TFOT to after TFOT is acceptable for both Conventional and Butaphalt(tm) Processing.

The last area we will discuss deals with the newer test methods as developed by the Strategic Highway Test Program (SHRP). These tests cumulate in a PG grading system. For our purposes, we will look at the PG grading system as a continuous grading system. A continuous grading is determined by the absolute value sum of the high and low PG grading values. In this study, 3.00% by weight of a styrenic block copolymer of a different physical structure and chemical ratio than those previously discussed was processed with a "typical" or "average" asphalt. The PG grading results in a high and a low Celsius temperature service value. These values for the Unmodified or Control asphalt, Conventional and Butaphalt(tm) Processing are given below in Table 6 below.

Table 6

Test Range	Control	Conventional	Butaphalt
High Value	+59	+69	+74
Low Value	-30	-29	-32
Continuous	89	98	106

These results illustrate conclusively that the Butaphalt(tm) process can create superior products in the PG grading system. Improvements are consistent with previous results presented in this discussion. Notice in particular the ability of the Butaphalt(tm) Process to significantly improve both the high and low end of the PG grading. These improvements are a desirable direction over the Control and that provided by the Conventional Process.

In conclusion, the use of Phenol-Aldehyde cross linking resins as reduced to practice in the Butaphalt(tm) Process (Patented) can provide useful tools to improving polymer modified asphalt.

